

Direct Electrolytic Refining of Lead Acid Battery Sludge

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Abstract: The direct electrorefining of anode particles obtained from lead acid battery sludge to produce electrolytic lead powder without application of the conventional leaching process is the aim of this work. To create this target, exhausted lead acid batteries were crushed to smaller particles and separated from the internal and external plastic covers and fed into a titanium nets basket which acts as the anode in the electrolytic cell. Two pure lead permanent cathode sheets together with the Ti-anode basket were immersed in an acidified leach liquor electrolyte containing 1.24 wt% HCl acid and 2.2 wt% Pb ions. Different parameters were investigated, such as addition of NaCl to the electrolyte, electrolyte stirring rate, electrolysis mode (electrorefining or electrowinning), and presence of suspended $PbCl_2$ particles in the electrolyte. Electrolytic lead powders with a dispersed shape with about 0.7% Ti were obtained. The obtained results indicated that the electrorefining technique is better than electrowinning with both cathodic current efficiency and powder productivity, while the energy required for the electrowinning process is lower. The electrorefining process was carried out with cathodic current efficiency up to 64.69% and specific electrical energy demand in the range from 2.598 to 3.827 kWh/kg Pb with powder productivity up to 2.5 g/A.h.

Keywords: Lead acid battery sludge, Particulate anode, Electrorefining, Electrolytic lead powder

Direkte elektrolytische Raffination von Bleibatterie-Schlamm

Zusammenfassung: Die direkte elektrolytische Raffination von Anodenpartikel, die aus dem Schlamm der Bleibatterie zur Erzeugung von elektrolytischem Bleipulver ohne Anwendung des konventionellen Laugungsprozesses gewonnen wird, ist das Ziel dieser Arbeit. Die verbrauchte Bleibatterie wurde gebrochen und in einen Titankorb gefüllt, der als inerte Anode dient. Zwei Bleibleche als permanente Kathoden sowie der gefüllte Titankorb wurden in eine Elektrolysezelle mit einer Lösung, die 2,2 Gew.-% Blei und 1,24 Gew.-% Salzsäure enthielt, eingetaucht. Verschiedene Faktoren, wie die Zugabe von NaCl zur Elektrolyten, Rührgeschwindigkeiten des Elektrolyts, Art des Elektrolyseprozesses (Elektrorefination und Elektrogewinnung) und der Einfluss von suspendierten $PbCl_2$ Partikeln im Elektrolyt, wurden untersucht. Es wurde Bleipulver mit 7% Ti in feinst verteilter Form erzeugt. Die Ergebnisse zeigen, dass das Elektrorefinationsverfahren die bessere Methode ist als das Elektrogewinnungsverfahren sowohl in Hinblick auf die Kathodenstromeffizienz als auch auf die Produktivität. Jedoch ist der Energiebedarf für das Elektrogewinnungsverfahren niedriger. Das Elektrorefinationsverfahren wurde bei einer kathodischen Stromdichte von 64,69% und einem spezifischen Energiebedarf von 2,598 bis 3,827 kWh/kg mit einer Produktivität für das Pulver von 2,5 g/A.h durchgeführt.

Schlüsselwörter: Bleisäurebatterieschlamm, Teilchenförmige Anode, Elektrorefination, Elektrolytisches Bleipulver

1. Introduction

Lead acid batteries are considered as the chief source of lead scrap together with the other sources such as cable coverings, pipe, sheet, and other lead-bearing metals.

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Fig. 1: A photo of lead acid battery sludge particles

TABLE 1:

Percentage composition of the utilized lead acid battery sludge before and after experiment

Component	Wt %	
	Before experiment	After experiment
Pb	79.6	91.7
Ti	0.0376	3.85
Si	4.84	ND*
Cl	ND*	2.88
Sb	14.9	0.703
Bi	ND*	0.411
Ca	0.623	0.252
Fe	ND*	0.244
S	ND*	ND*

*ND not determined

Over 70% of the world's total output of lead is consumed in the manufacture of lead-acid storage batteries [1]. At the end of their life, such batteries are readily collected and become the major feed to the secondary lead industries. Battery scrap from the automobile sector accounts for 80% of old scrap recycled as secondary lead raw material [1].

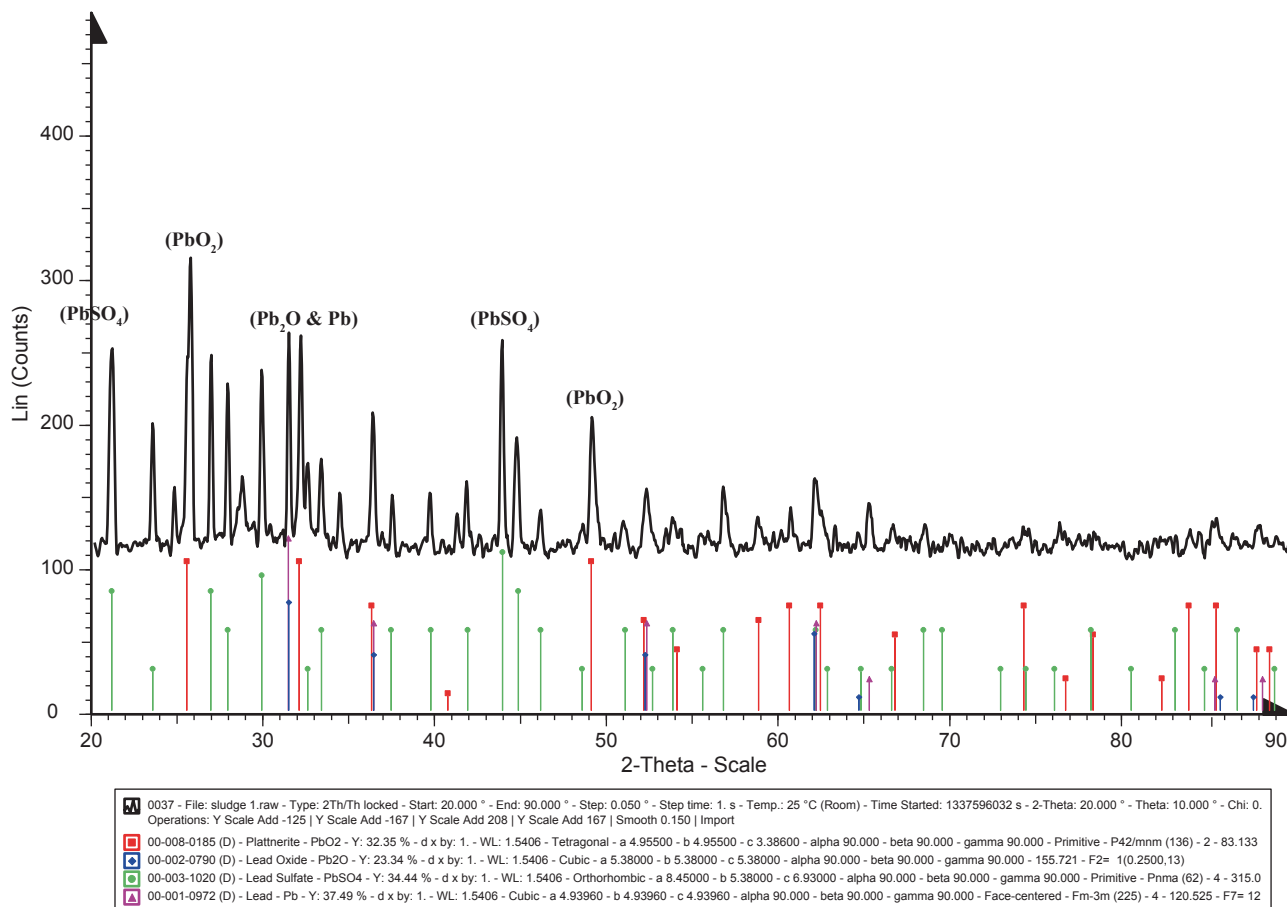


Fig. 2: XRD pattern of lead acid battery sludge

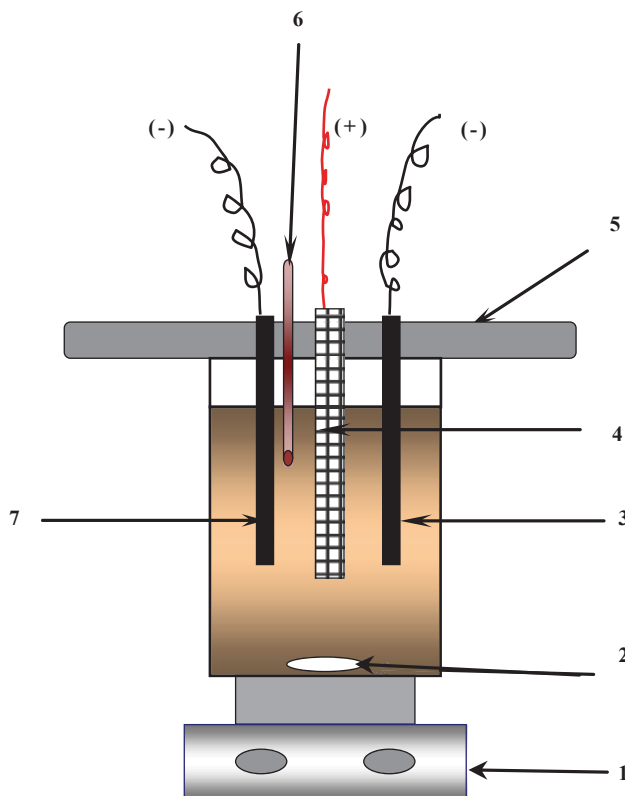


Fig. 3: Details of bench scale experimental setup. 1 hot plate with magnetic stirrer, 2 rotating fish, 3 Pb-cathode 1 (-), 4 Ti basket with sludge particles anode (+), 5 stand & cell cover, 6 thermometer, 7 Pb-cathode 2 (-)

A standard lead acid battery contains a significant amount of active mass (PbO_x , PbSO_4) with about 38.5% [1]. This active mass forms the sludge after exhausting the battery.

Dead batteries are broken into small pieces to separate the lead containing components from the remainder of the battery, which are mainly plastics. Fractions of cleaned plastic, such as polypropylene, are recycled into battery cases or other products. Moreover, the dilute sulfuric acid is either neutralized for disposal or recycled for the local acid market. The lead containing components are obtained in the form of a pasty product (battery sludge). However, the battery sludge consists mainly of salts and oxides of lead in particles form, together with an amount of water. The predominant components in the battery sludge are lead (II) sulphate (55–60%), lead (II) oxide and lead (IV) oxide (20–25%) and metallic lead (1–5%) [2].

Pyrometallurgical smelting processes are still currently in use and comprise over 90% of the lead recovery from spent lead acid batteries [3]. Several papers and patents have focused on this technology [4–9]. These processes are under severe criticism, especially due to SO_2 emission from the decomposition of PbSO_4 at elevated temperatures ($>1000^\circ\text{C}$) and lead emissions from fuming at these high temperatures. Because of the tight environmental regulations in the world, environmentally friendly hydrometallurgical processes have been developed to treat lead acid battery scrap, particularly the battery paste/sludge [10–17]. The objective of the processes in most cases is to fix the sulphur as a harmless sulphate and to put the lead into a suitable solution for electrolytic recovery. From the environmental point of view, lead recovery from battery

Fig. 4: Views of the used electrolytic cell (a) and the Ti anode basket filled with sludge particles (b). 1 hot plate with magnetic stirrer, 2 5 liter backer glass filled with electrolyte, 3 Ti anode basket, 4 digital multimeter connected to laptop, 5 two starting lead cathode sheets, 6 DC supplier

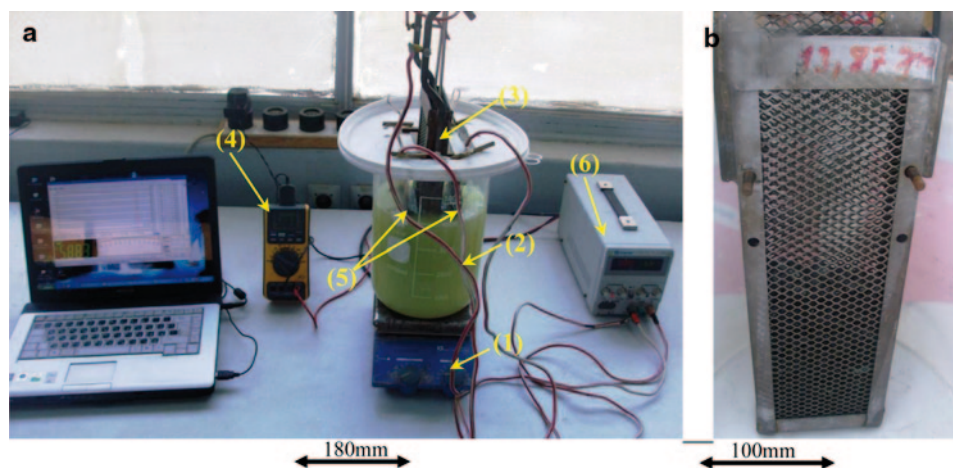


TABLE 2:

Electrolysis data of the effect of NaCl concentration on electrorefining of lead acid battery sludge

NaCl concentration	Current density	Electrolyte temperature	Electrolyte stirring rate	Duration	Average cell voltage	Cathodic deposition	Current efficiency	Sp. Energy demand	Productivity
[g/l]	[A/m ²]	[°C]	[rpm]	[min]	[V]	[g]	[%]	[kWh/ kg]	[g/A. h]
Without	400	60	350	31	8.332	9	56.34	3.827	2.177
50	400	60	350	30	6.495	10	64.69	2.598	2.500
100	400	60	350	30	6.515	10	64.69	2.606	2.500

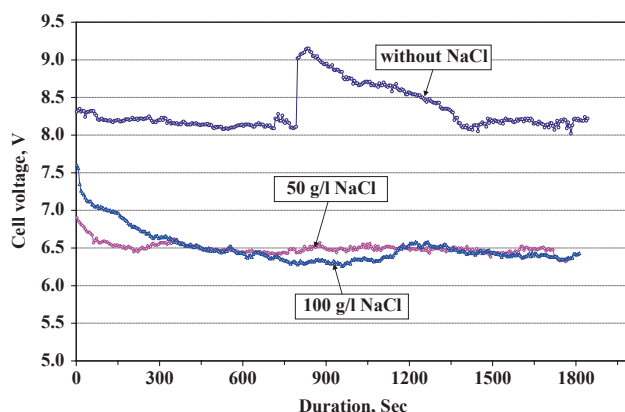


Fig. 5: Cell voltage against duration of the electrorefining of lead acid battery sludge at different concentrations of NaCl in electrolyte [60°C, 400 A/m², 350 rpm]

sludge via hydrometallurgical and/or electrometallurgical processes looks very attractive. The application of cementation [18] or electrowinning [19–20] processes of metallic lead after hydrometallurgical dissolution of lead acid battery sludge and/or of electrorefining technique using fluidized bed of sludge anode particles [21] could be a good solution for the treatment of sludge in the ordinary aqueous solvents.

The aim of this research is to provide an alternative process for the recovery of electrolytic lead powder from battery sludge in one step only without the application of the conventional acidic or basic leaching technique. To accomplish the objective, the sludge particles were separated from both internal/external plastic covers and metallic lead grids. Subsequently, they were placed in a titanium basket, which acts as the carrier and the positive electrode (anode) in the employed electrolytic cell. Two lead sheets used as starting cathodes together with titanium anode basket were positioned in an electrolytic cell containing electrolyte composed of dilute HCl solution (1.24%) and lead ions (2.2%) together with NaCl solution. Finally, the influence of different experimental parameters such as NaCl concentration in the electrolyte, electrolyte stirring rate, presence of suspended PbCl₂ particles in the electrolyte, and electrolysis mode on the yield of lead powder is studied.

2. Experimental Details

2.1 Materials

Lead acid batteries were broken to smaller particles and separated from the internal and the external plastic covers. Sludge particle sizes in the range of 4–8 mm (Fig. 1) were put in a titanium basket and employed as the anode in the electrolytic cell. The different components and phases that exist in the sludge particles were examined by X-ray fluorescence (XRF) (Rigaku XRF-NEXCG, Japan) and X-ray diffraction (XRD) analyzer (D5000 powder diffractometer, Germany) and are presented in Table 1 and

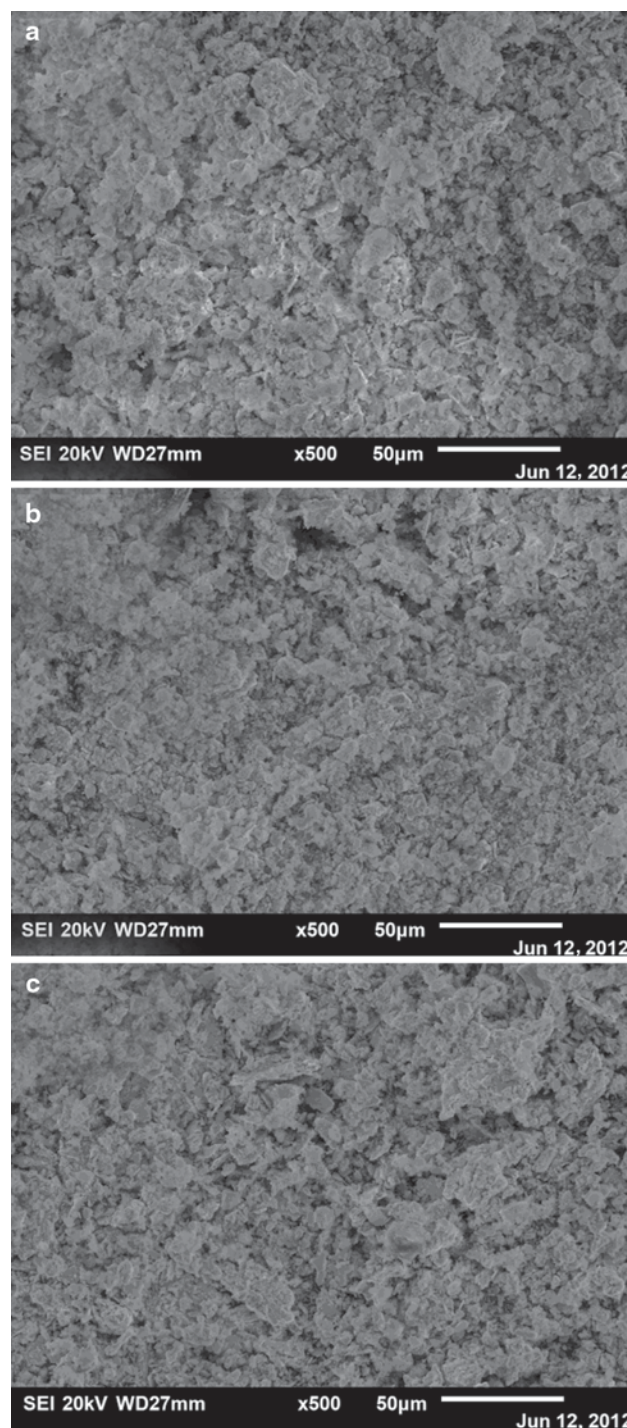


Fig. 6: SEM micrographs of the deposited lead powders from electrorefining of lead acid battery sludge at 60°C, 400A/m² and 350 rpm (magnification X500), a without NaCl, b with 50 g/l NaCl, c with 100 g/l NaCl

Fig. 2 respectively. Fine powders of the battery sludge obtained during crushing step were dissolved in a dilute HCl solution at 70°C for 24 hrs to give the required leach liquor electrolyte with the composition of 1.24 wt% HCl and 2.2 wt% Pb.

TABLE 3:

Electrolysis data of the effect of electrolyte stirring rate on electrorefining of lead acid battery sludge

Electrolyte stirring rate	NaCl concentration	Electrolyte temperature	Current density	Duration	Average cell voltage	Cathodic deposition	Current efficiency	Sp. Energy demand	Productivity
[rpm]	[g/l]	[°C]	[A/m ²]	[min]	[V]	[g]	[%]	[kWh/ kg]	[g/A. h]
350	100	60	400	30	6.515	10	64.69	2.606	2.500
600	100	60	400	31	6.916	9	56.34	3.176	2.177

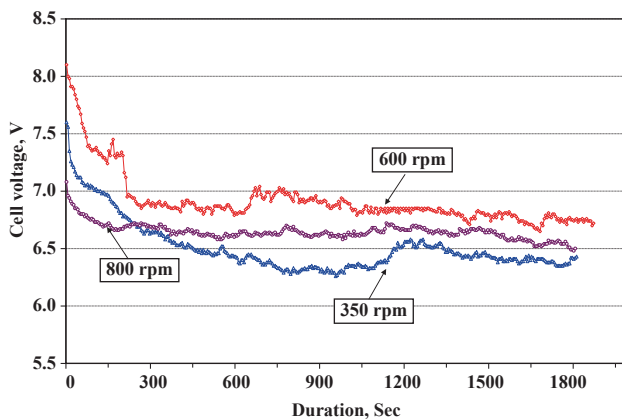


Fig. 7: Cell voltage against duration of the electrorefining of lead acid battery sludge at different electrolyte stirring rates [400 A/m², 60 °C, 100 g/l NaCl]

2.2 Experimental Apparatus and Procedure

The sketch of the bench scale experimental setup used for electrorefining experiments is shown in Fig. 3, while the actual view of the different applied devices is illustrated in Fig. 4a. Sludge particles were put in a titanium basket, which has the dimension of 100 mm width, 100 mm active height, and 30 mm thickness with 5 mm net openings average size (Fig. 4b). Two lead sheets with the dimensions of 100 mm width, 100 mm active height and 3 mm thickness were used as starting permanent cathodes. Both Ti anode basket filled with sludge particles and lead cathodes were inserted in a 5 liter beaker glass, which was filled with the previously prepared electrolyte. For the electrowinning experiment, one graphite anode plate with the dimension of 100 mm width, 100 mm active height, and 8 mm thickness together with the same lead cathode sheets applied in the electrorefining experiment were used. The electrodes were suspended in the cell with an anode/cathode separating distance of 25 mm. A hot plate with magnetic stirrer (K...RH basic IKA LABORTECHNIK, Germany) was used for heating up and agitating the electrolyte. The direct current was supplied to the electrodes by a power supplier (GW Instek, DC Power supply sps-1820, Taiwan). The output cell voltage was directly recorded to the computer using digital multimeter VA18B with PC-Link computer software.

The electrodeposited powders were extensively washed in water, dried, weighed, and analyzed using scanning electron microscopy (JEOL JSM-6360LA, Japan), X-ray fluorescence (XRF), and XRD analyzers.

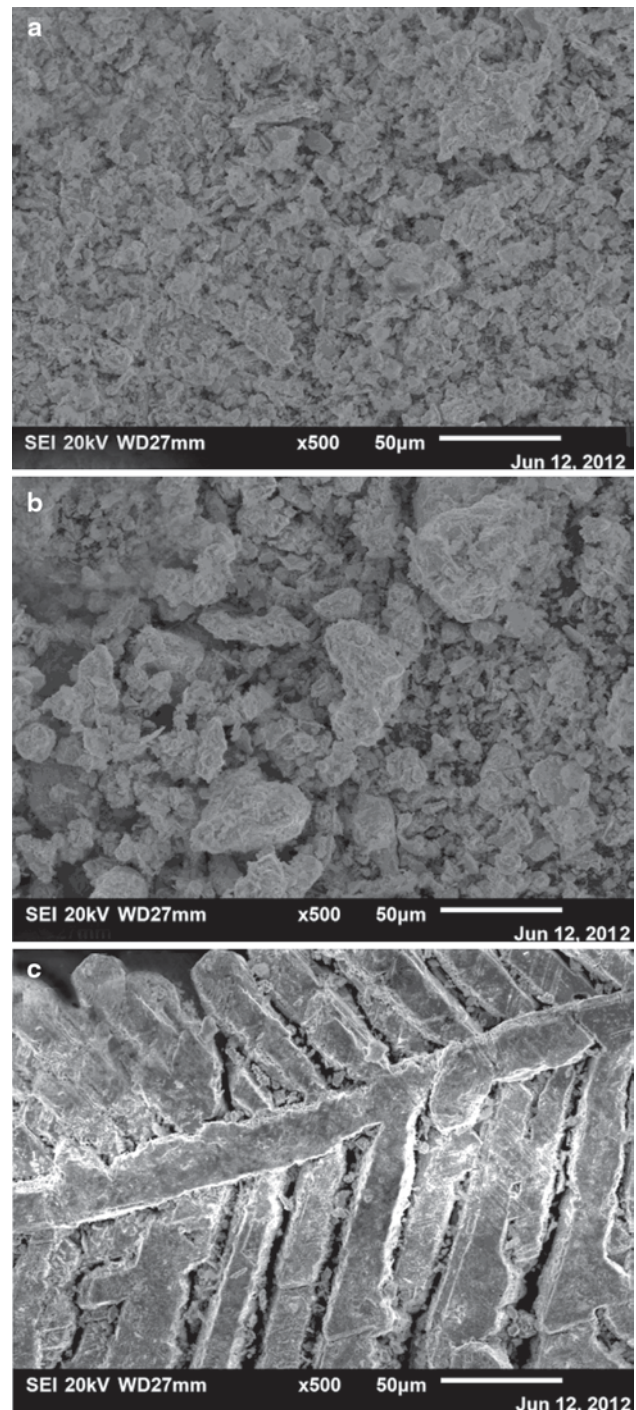


Fig. 8: SEM micrographs of the deposited lead powder from electrorefining of lead acid battery sludge at 400 A/m², 60 °C and 100 g/l NaCl (magnification x500), **a** at 350 rpm, **b** at 600 rpm, **c** at 800 rpm

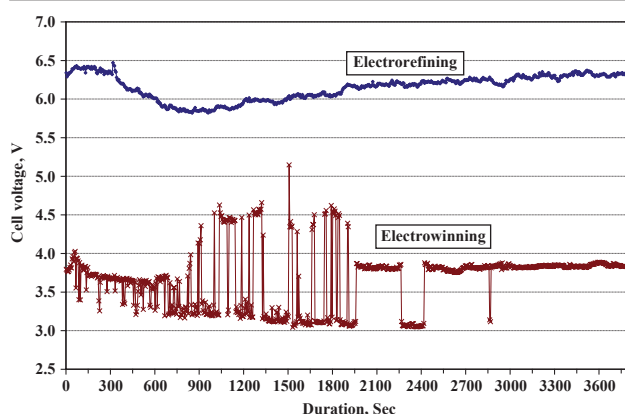


Fig. 9: Cell voltage against duration of the electrolysis process of both electrorefining and electrowinning techniques for electrodeposition of lead powder from lead acid battery sludge [400 A/m², 350 rpm, 60 °C and 100 g/l NaCl]

3. Results and Discussion

Different factors were extensively studied to show their effect on the electrorefining process of lead acid battery sludge to obtain electrolytic lead powder at 400 A/m² and 60 °C. The main factors studied are electrolyte concentration of NaCl, electrolyte stirring rate, electrolysis mode, and the presence of suspended PbCl₂ particles in the electrolyte.

3.1 Effect of Addition of NaCl to the Electrolyte

From the results shown in Table 2 and Fig. 5, it is obvious that the addition of NaCl to the electrolyte has a positive effect on the all parameters of the electrorefining process. Both the cathodic current efficiency and powder productivity were increased, while the specific energy demand was decreased. This can be due to the increase of electrolyte conductivity resulting from the addition of NaCl. It is also clear that the increase of NaCl concentration in the electrolyte from 50 g/l to 100 g/l has no significant effect on the process parameters. The lower values of current efficiency (<65%) may be due to the lower concentration of lead ions in the electrolyte, where the saturation limit of PbCl₂ is very low (9.9 g/l at 20 °C and 33.4 g/l at 100 °C) [22]. This low limit causes a decrease in the electrodeposition of metallic lead and deposits Cl₂ gas instead of lead.

The higher value of cell voltage at the beginning of electrorefining process when NaCl is added could be due to the hydrogen overvoltage of starting lead cathodes, while its decrease in the later stages of the process could be explained by the deposition of lead powder on the cathode surface, which gradually decreases the distance between anode and cathode and consequently causes a decrease in electrical resistance of the electrolyte. The peak in the upper curve in Fig. 5 (without addition of NaCl) is due to the removing of the deposited powder from the surface of the lead cathode, which causes an increase in the distance between anode and cathode and increases the Ohmic resistance of the electrolyte and consequently increases the cell voltage.

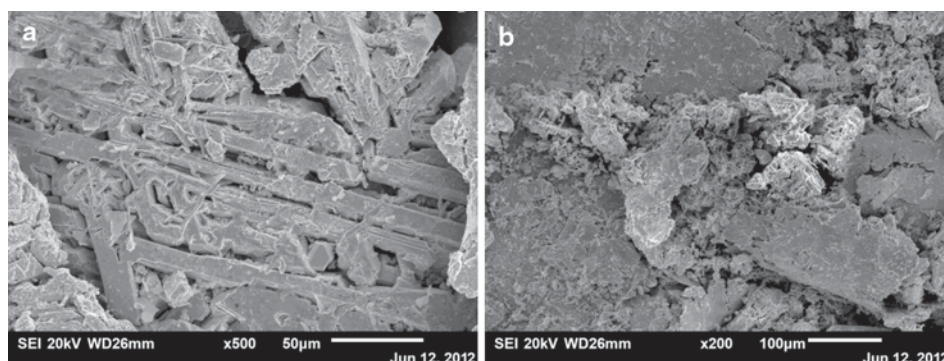
SEM micrographs of the electrodeposited lead powder are illustrated in Fig. 6 and indicate that the electrodepos-

TABLE 4:

Electrolysis data of the effect of electrolysis mode on electrometallurgical treatment of lead acid battery sludge particles

Elec- trolysis Technique	NaCl con- centration	Current density	Electrolyte temperature	Electrolyte stirring rate	Duration	Average cell voltage	Cathodic deposition	Cathodic current efficiency	Sp. Energy demand	Productiv- ity
	[g/l]	[A/m ²]	[°C]	[rpm]	[min]	[V]	[g]	[%]	[kWh/ kg]	[g/A. h]
Electro- refining	100	400	60	350	63	6.151	18	55.44	2.870	2.143
Electro- winning	100	400	60	350	63	3.659	13	40.17	2.357	1.553

Fig. 10: SEM micrographs of electrodeposited lead powder from both electrorefining (a) and electrowinning (b) techniques (400 A/m², 350 rpm, 60 °C, 100 g/l NaCl)



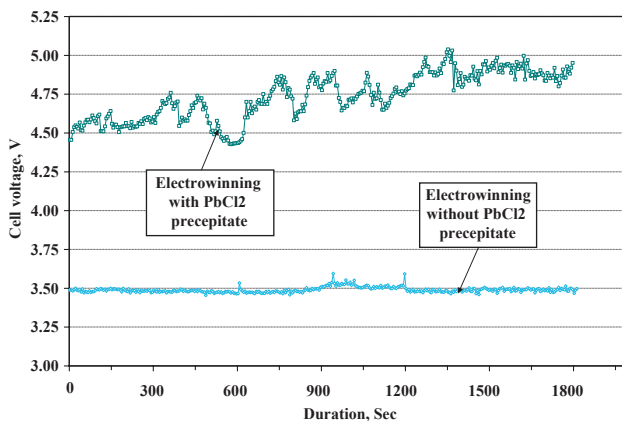


Fig. 11: Cell voltage against duration of the electrolysis process of electrowinning of lead powder from lead acid battery sludge leach liquor solution with and without PbCl_2 suspended particles [400 A/m^2 , 600 rpm, 60 °C, 100 g/l NaCl]

ited lead powders are in a dispersive form. The addition of NaCl to the electrolyte has no clear effect on the particle size or the shape of the resulting powders.

3.2 Effect of Electrolyte Stirring Rate

The increase of electrolyte stirring rate from 350 rpm to 800 rpm has a bad effect on cathodic current efficiency, specific energy demand, and lead powder productivity, as shown in Table 3, apart from its strong effect on the corrosion of the Ti-anode basket. There is no sharp difference between the cell voltages of each experiment using the different stirring rates, as shown in Fig. 7.

SEM micrographs of the electrodeposited lead powders from electrorefining of lead acid battery sludge applying different stirring rates at 400 A/m^2 , 60 °C and 100 g/l NaCl are presented in Fig. 8. They show the dispersed shape of lead powders with a sharp increase in particle size when the stirring rate is increased. Powders with coarse dendritic shape were obtained when the stirring rate is increased to 800 rpm.

3.3 Effect of Electrolysis Mode

Table 4 and Fig. 9 show the effect of both electrorefining and electrowinning techniques on the electrodeposition of lead powders from lead acid battery sludge particles. Table 4 indicates that both current efficiency and powder productivity show an obvious increase when the electrorefining technique is applied. This can be attributed to the continuous feeding of lead ions to the electrolyte during the electroleaching of sludge anode particles in the electrorefining process, while the resulting cell voltage and specific energy demand is increased. This can be attributed to the lower electrical conductivity of non-metallic sludge particles, which form the packed bed anode in comparison to graphite anode plate in the case of the electrowinning process. The vibration at the beginning of the electrowinning curve in Fig. 9 can be due to the electrical contact and the presence of the suspended PbCl_2 precipitates in the electrolyte apart from the behavior of electrowinning process.

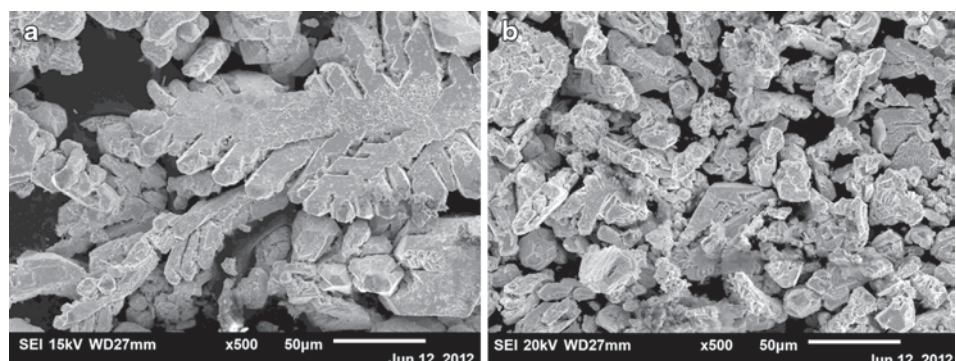
SEM micrographs of the electrodeposited lead powders from lead acid battery sludge using electrowinning and electrorefining techniques at 400 A/m^2 , 60 °C, 350 rpm, and 100 g/l NaCl are presented in Fig. 10. They show the dispersed shape of lead powders obtained from the electro-

TABLE 5:

Electrolysis data of the effect of the presence of suspended PbCl_2 particles in the electrolyte on *electrowinning* process

PbCl_2 slurry	NaCl concentration	Current density	Electrolyte temperature	Electrolyte stirring rate	Duration	Average cell voltage	Cathodic deposition	Cathodic current efficiency	Sp. Energy demand	Productivity
	[g/l]	[A/m^2]	[°C]	[rpm]	[min]	[V]	[g]	[%]	[kWh/ kg]	[g/A. h]
with	100	400	60	600	30	4.735	4	25.87	4.735	1.000
without	100	400	60	600	30	3.489	4	25.66	3.518	0.992

Fig. 12: SEM micrographs of electrodeposited lead powder from electrowinning of lead acid battery sludge leach liquor solution with (a) and without (b) suspended PbCl_2 particles (magnification $\times 500$) [400 A/m^2 , 350 rpm, 60 °C, 100 g/l NaCl]



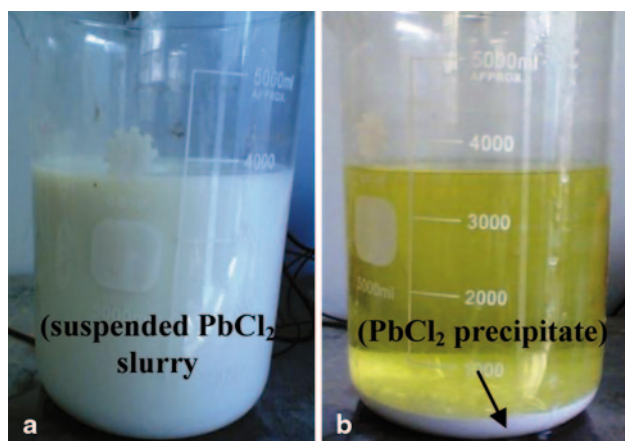


Fig. 13: Photos of beaker glass filled with suspension of PbCl_2 (a) and with bottom precipitated PbCl_2 particles (b)

winning technique, while coarse dendritic powders were obtained when the electrorefining technique was applied.

3.4 Effect of Presence of Suspended PbCl_2 Particles in the Electrolyte

Electrowinning process data of the effect of the presence of suspended PbCl_2 particles in the electrolyte on the lead powder production from lead acid battery sludge leach

liquor solution is presented in Table 5 and Fig. 11. It is shown that the utilization of electrolyte solution with no PbCl_2 suspended particles is much better for cell voltage and specific energy demand, while the cathodic current efficiency and powder productivity is about the same in both cases. This can be attributed to the bad effect of suspended non-conductive PbCl_2 particles on the electrical conductivity of the electrolyte, which causes a gradual increase the cell voltage and also a vibration in the curves. A gradual rise in the values of cell voltage from start of the experiments to the end can be due to the gradual increase in concentration of PbCl_2 particles in the electrolyte.

The SEM of the electrodeposited lead powders from electrowinning of leach liquor solution obtained from lead acid battery sludge with and without PbCl_2 suspended particles are illustrated in Fig. 12. It is shown that removing PbCl_2 suspended particles from the electrolyte has a strong effect on the size and shape of the obtained powders. When PbCl_2 suspended particles are removed, finer powders with dispersed shape were obtained, while the presence of such particles causes a formation of coarse powders with dendritic shape.

The view of the resulting electrolyte after leaching of lead acid battery sludge containing PbCl_2 suspended particles is illustrated in Fig. 13a. The view after precipitation of PbCl_2 particles in the bottom of the beaker glass is illustrated in Fig. 13b.

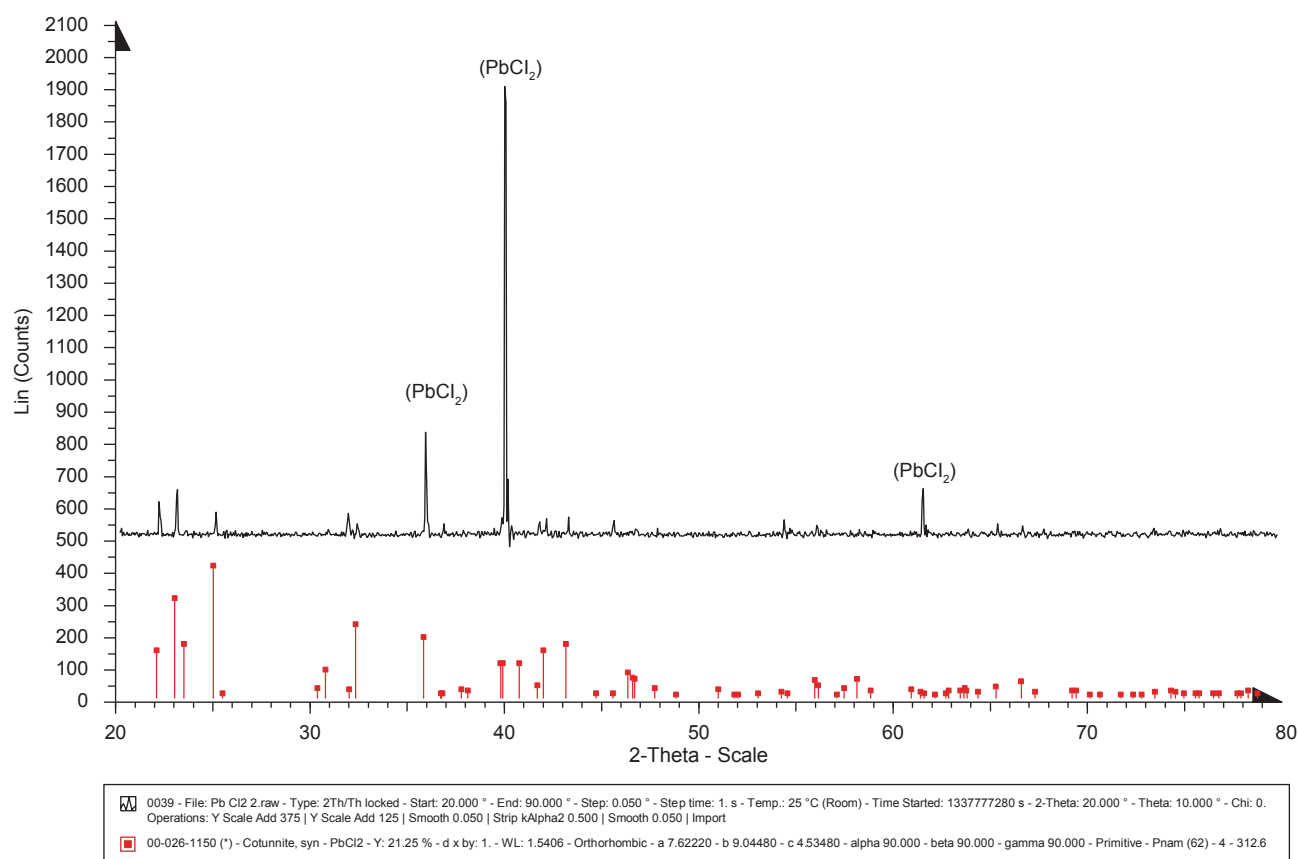


Fig. 14: XRD pattern of PbCl_2 precipitates formed in electrolyte during electrorefining of lead acid battery sludge

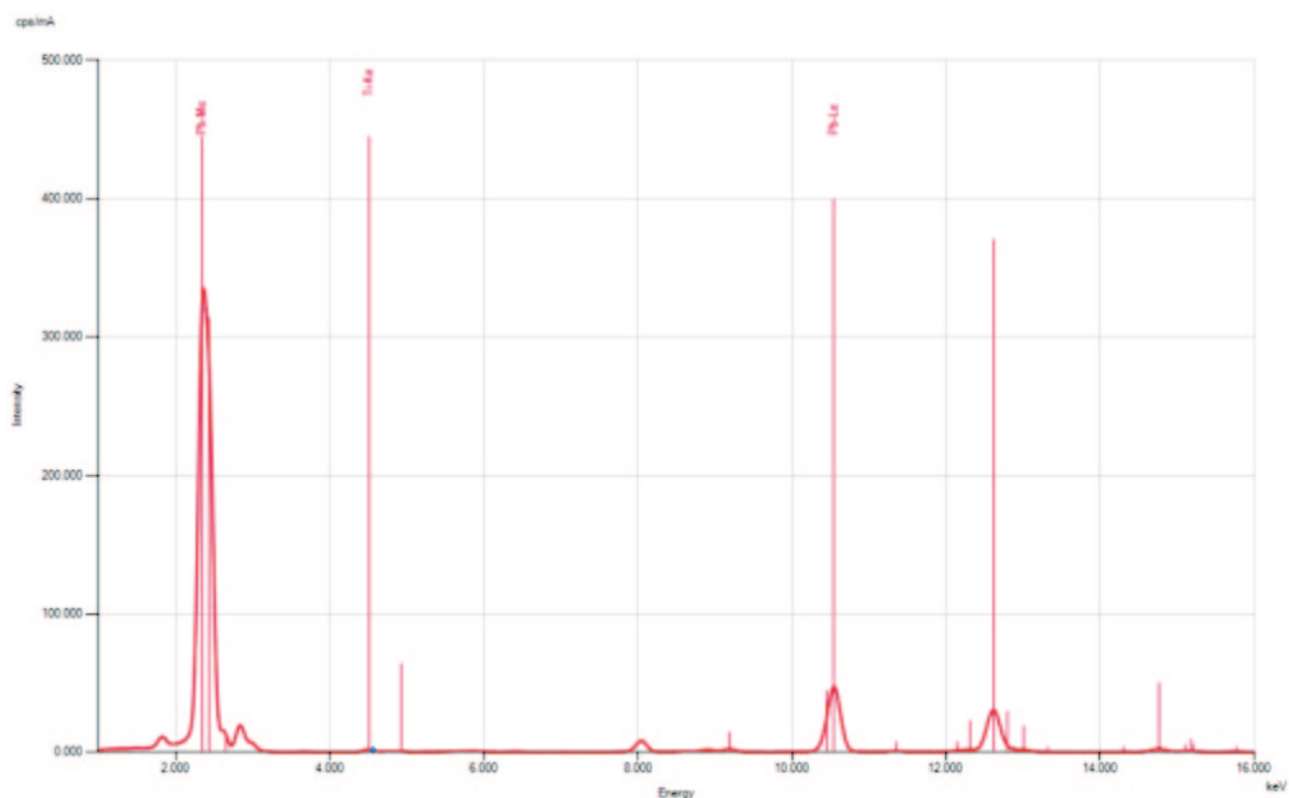


Fig. 15: XRF spectra of the electrodeposited lead powder

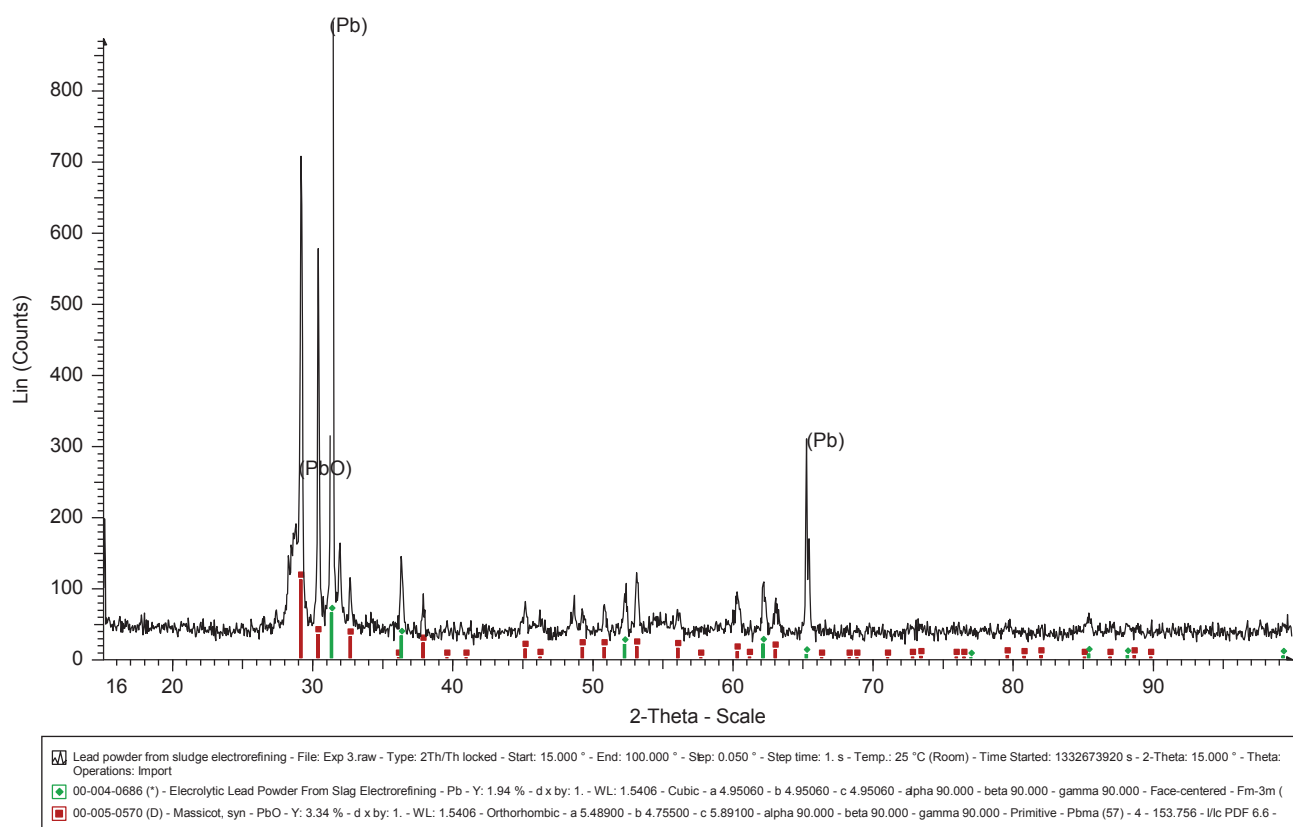


Fig. 16: XRD pattern of the electrodeposited lead powder

Precipitated PbCl_2 particles were investigated by using an XRD analyzer and the chart obtained is presented in Fig. 14. It is shown from the pattern that the precipitated particles were extremely pure PbCl_2 phase without any other contaminations. The reason is that the leachate solution exceeded the saturation limit of PbCl_2 , which is about 9.9 and 33.4 g/l in water at both 20 and 100 °C respectively, while its solubility in dilute HCl acid is very slight. The formation of PbCl_2 in the electrolyte can result from the reaction of hydrochloric acid with both lead dioxide ($\text{PbO}_2(\text{s}) + 4 \text{HCl} (\text{PbCl}_2(\text{s}) + \text{Cl}_2 + 2 \text{H}_2\text{O})$) and also lead oxide ($\text{PbO}(\text{s}) + 2 \text{HCl} (\text{PbCl}_2(\text{s}) + \text{H}_2\text{O})$). Lead chloride precipitates can also be formed by the action of chlorine gas on the electrodeposited lead metal powders ($\text{Pb} + \text{Cl}_2 \rightarrow \text{PbCl}_2$) [22].

XRF analysis of the electrodeposited powders is illustrated in Fig. 15 and indicates that lead powders with about 0.6–0.7 % Ti were obtained during the electrorefining process, which resulted from the partial corrosion of Ti-anode basket especially at a higher rate of electrolyte stirring, while pure lead powder (100 % Pb) was obtained from electrowinning technique. The appearance of some lead oxide (PbO) in the deposited powder, as proved in Fig. 16, may result from oxidation of the outer surface of the powder during its drying in normal atmosphere. This can be avoided when the drying step is carried out in an inert atmosphere.

4. Conclusions

Lead acid battery sludge can be directly electrorefined by using the packed bed electrolysis technique at 400 A/m² and 60 °C to deposit electrolytic lead powder. Different factors were studied such as addition of NaCl to the electrolyte, electrolyte stirring rate, presence of PbCl_2 suspended particles in the electrolyte, and electrolysis mode (electrorefining and electrowinning). The obtained results indicated that:

1. The addition of NaCl to the electrolyte has a positive effect on all the process parameters, due to the increase in electrical conductivity of the electrolyte, while the increase in its concentration from 50 to 100 g/l has no obvious effect.
2. The increase in stirring rate of the utilized electrolyte and the presence of suspended PbCl_2 particles in the electrolyte have a negative effect on the electrorefining process, which can be attributed to the lowering of the electrical conductivity of the electrolyte because of the presence of non-metallic, non-conductive PbCl_2 particles suspended in the electrolyte. So the precipitation of the suspended particles and the decrease of the electrolyte stirring rate are favored to avoid distribution of PbCl_2 particles in the electrolyte bath.
3. The application of only a one-step technique using direct electrorefining process is better than utilizing the two-step technique using acidic or basic leaching medium followed by electrowinning process, where the cathodic current efficiency and productivity is better in the one-step process, while the specific energy

demand is better only in the electrowinning step and it is expected to be higher when the energy required for the leaching step is considered.

5. Acknowledgements

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